

# **DECOMPOSITION KINETIC OF GREASES BY THERMAL ANALYSIS**

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## **ABSTRACT**

Pressure Differential Scanning Calorimeter (PDSC) is a thermal analytical technique for evaluating oxidation-thermal stability of polymer materials including lubricating greases using the differential heat flow between sample reference thermocouples under various temperatures and pressures. The ASTM D 5483 test method is one of acceptable PDSC techniques to evaluate the grease oxidation stability. In a research effort, a decomposition kinetic model was developed to predict grease high temperature life using ASTM D 5483 PDSC technique. This kinetic model can predict grease oxidation life at the various temperatures and the degree of oxidation using their activation energy. Also, it was found that this kinetic model has a limited correlation to the results from ASTM D 3527 grease life test. This kinetic model can therefore be used to predict the high temperature grease life within certain constraints.

## **INTRODUCTION**

Lubricating greases are essential components in a daily operation of vehicles and equipment. These greases are originally formulated to reduce friction of moving mechanical parts such as bearings. For the last several decades, many researchers had contributed their efforts to develop a modeling system that can predict grease high temperature life. Unfortunately, there is no modeling system available at this time to predict grease life. Currently, the high temperature life of grease is estimated using the ASTM D 3527 test method, Life Performance of Automotive Wheel Bearing Grease. The disadvantage of this method is its poor test precision, long endurance testing time, and questionable correlation with field vehicle under operating conditions<sup>1</sup>. For this reason, it has not been extensively utilized in grease research and development or in the development of specifications. Therefore, a study is needed to define, measure, and develop a modeling system to predict a grease decomposition life.

Pressure Differential Scanning Calorimetry (PDSC) is a thermal analytical technique to evaluate oxidation-thermal stability of lubricants using the differential heat flow between sample and reference thermocouple under various temperatures and pressures. It measures thermodynamic properties and oxidation life of lubricants. The major advantages of this technique are to reduce the volatilization of additives under a high

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pressure, increase the concentration of reacting gases, and require a very small sample. This allows lower test temperatures to be used for testing or provides shorter testing times. Recently, this technique has become the most widely used in the polymer quality control and research applications particularly useful for determining vapor pressures and the oxidation stability of lubricants<sup>2,3</sup>.

In 1990, U.S. Army had developed a new oxidation stability test method for greases using the PDSC technique<sup>4</sup>. Later, this method became adopted as the ASTM D 5483, Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry. This test method is currently used to determine the oxidation stability of greases and its shelf-life determination. The kinetic model associated with this method has been developed to predict induction times of greases at various temperatures within the PDSC test. However, it was found that the kinetic equation has a limited capability to predict the induction time due to its inaccurate activation energy determination. In addition, this model does not have a capability to determine the conversion of oxidation in a PDSC test. It needs a modification and further development to improve its prediction capability. For this reason, a study was initiated to develop a kinetic model that can predict the high temperature life of a grease within a short time. This new kinetic model not only provides a good predictability of oxidation life within a PDSC test, but it has a good correlation to the existing grease life test such as the ASTM D 3527 test. This paper will detail how to develop a decomposition kinetic model, its correlation to a bearing test and applications.

## **KINETIC MODEL OF GREASE OXIDATION**

Oxidation of lubricating greases is thermodynamically irreversible and is defined as an exothermic reaction<sup>5</sup>. The deterioration of grease generally results from oxidation reactions, which increase as temperature is raised<sup>6</sup>. The detailed oxidation mechanism of grease is not yet established due to chemical complexity of its formulation and the complexity of oxidation reactions themselves. In many oxidation test methods that have been developed, the ASTM D 5483 test method has been widely utilized to determine the oxidation stability of greases using a PDSC. This test method was designed to measure induction times at various temperatures under a pressurized oxygen environment. In this procedure, the degree of oxidation stability of greases at given temperature is determined by an oxidation induction time. A kinetic equation associated with this procedure is used to predict an oxidation induction time of grease at the various temperatures<sup>4</sup>. This equation has been developed based on the thermodynamics and chemical reaction theory. However, it was found that the kinetic equation has a limited capability to predict the induction time due to its inaccurate activation energy determination.

To improve its predictable capacity, a kinetic model was modified and further developed using a first-order kinetic equation which is independent of the initial concentration of sample. For the study, ten grease samples were selected and tested according to the ASTM D 5483 test method. Table 1 provides grease identification and their physical properties. Most greases are known as high dropping point greases and

currently used in the rolling element bearing applications. In searching for a rate equation, PDSC data obtained from Grease A and B listed in Table 2 were plotted on Figure 1 using the Arrhenius model, which has a reciprocal scale for absolute temperature and a natural logarithmic scale for induction time. This Arrhenius plotting technique is often used to determine whether the reaction can be fitted into the first-order rate equation which gives a reasonably straight line for this plotting. The resulting graphs show the data points fall on straight lines and the slopes of these lines, proportional to the activation energy, are not identical. Generally, the activation energy (E) of grease at given reaction is considered as constant and independent from temperatures<sup>4</sup>. The reaction with high activation energies is much more temperature-sensitive than those of low activation energies<sup>7</sup>. The first-order kinetic equation may be expressed in terms of fractional conversion X and the rate constant k which depends on the temperatures.

$$t = -\ln(1-X)/k \quad [1]$$

where  
t: induction time

The rate constant (k) of this equation is usually associated with the Arrhenius' law, which is based on a theoretical relationship between chemical reaction rates and temperatures<sup>8</sup>.

$$k = k_0 e^{-\frac{E}{RT}} \quad [2]$$

$k_0$  is a frequency factor and R is a universal constant (8.314 J/mol. K). E is denoted as activation energy. In this equation, raising the temperature increases the reaction rate (k). To make a kinetic model, Equation 2 is substituted into Equation 1, resulting in equation 3.

$$t = -\left(\frac{1}{k_0}\right) \ln(1-X) e^{\frac{E}{RT}} \quad [3]$$

The term  $-\left(\frac{1}{k_0}\right) \ln(1-X)$  is assumed constant and denoted as A. After taking the natural logarithm, Equation 4 can be expressed in Arrhenius logarithmic form:

$$\ln t = \ln A + E/RT \quad [4]$$

This kinetic equation represents the negative straight line respect to 1/T and its differential equation is as follow:

$$d \ln t / d (1/T) = E/R \quad [5]$$

E/R represents a slop of the Arrhenius equation and can be calculated based on the experimental data. In a two-point calculation method, the activation energy (E) at given reaction can be determined using oxidation induction times obtained at two significantly

different reaction temperatures. The following equation requires two induction times ( $t_1$  and  $t_2$ ) measured at two different temperatures:

$$E = R \frac{T_1 T_2}{T_1 - T_2} \ln \left( \frac{t_1}{t_2} \right) \quad [6]$$

Then, the Arrhenius frequency factor can be calculated from the following equation:

$$k_o = - \ln (1-X_f)/t e^{E/RT} \quad [7]$$

This frequency factor ( $k_o$ ) is generally a constant at a given reaction and almost independent from temperatures<sup>7</sup>. In the PDSC test, the oxidation induction time is calculated at the end of exothermic reaction. The final conversion concentration ( $X_f$ ) can be assumed the same value at each PDSC test and denoted as 0.99. Then, the reaction rate constants ( $k$ ) at any temperatures can be calculated using Equation 2. For the decomposition kinetic model, Equation 3 can be rewritten by Equation 8.

$$t = \frac{4.6}{k_o} e^{\frac{E}{RT}} \quad [8]$$

where,

t: induction time, min

$k_o$ : Arrhenius frequency factor

E: activation energy

R: universal constant, 8.314 J/mol °K

T: absolute temperature, °K

This kinetic model was derived in Arrhenius form, and induction times vary only with the temperature. To verify the kinetic model developed, ten greases selected for this study have been examined and a correlation was made between the actual induction times and the predicted induction times. Table 3 summarizes predicted induction times for selected samples, frequency factor ( $k_o$ ) and their activation energies. Table 4 actually demonstrates this kinetic study using Grease A and shows the predicted induction times and their reaction constant ( $k$ ) at a series of temperatures. All data points shown in Table 2 for Grease A were plotted on Figure 2 to make a correlation with its predicted values from Table 4. The correlation coefficient ( $R^2$ ) was found to be 0.99.

The kinetic model also has a capability to predict oxidation conversion of grease using the first-order reaction equation. Table 5 lists the percentage oxidation conversion of Grease A at 180 °C. In addition, the conversion of degradation of grease can be calculated in respect with the original induction times at given reaction. Figure 3 shows the induction time profiles of new and used Grease A. It appears that their slopes (E/R) are almost identical. This implies their activation energies are not significantly changed during the degradation period. Based on this fact, the following equation can be derived to determine the percentage of degradation of grease under oxygen environment.  $k$  is a rate constant that calculated from the original grease (reference) at given reaction, while  $t$  is induction time measured from degraded grease.

$$\% \text{ degradation} = e^{-kt} \quad [9]$$

## **CORRELATION WITH ASTM D 3527 TEST METHOD**

The ASTM D 3527 test method covers a laboratory procedure for evaluating the high-temperature (160 °C) grease life under specified conditions. The significance of this method is that it differentiates among wheel bearing greases having distinctly different high-temperature characteristics only. The advantage in using this method is to comprehensively evaluate all individual physical properties of greases directly related to high temperature and shear, using a simulated front wheel bearing system and a dynamic laboratory bench-type test apparatus. For this reason, the method is often called as a dynamic oxidation stability test. The disadvantage of this method is its poor precision and a long testing time. Due to the poor test precision, this method does not have the capability to distinguish between the greases having similar high-temperature properties. In addition, the test results provide limited correlation to field performance. Unfortunately, there is no alternative dynamic test available with the standardized tests for greases.

To make a correlation between the ASTM D 3527 test and a PDSC kinetic model, ten greases selected for this study were tested according to the ASTM D 3527 test method. To increase reliability of data, four data points were generated for each sample and the average data were reported with induction times obtained from PDSC kinetic model in Table 6. For the study, PDSC data were generated at 180 °C instead of 160 °C. The reason is that the test temperature (160 °C) specified in the ASTM D-3527 test is measured from spindle hole in which the thermocouple is inserted, resulting in a temperature gap of about 20 °C between the chamber and spindle. It appears that the test temperature is closer to the chamber temperature instead of the spindle temperature because the test specimen (wheel bearing hub system) is fully open in the chamber and the heat transfer is facilitated by hot air in the chamber. Therefore, the actual test temperature of ASTM D 3527 test method is assumed to be higher than 160 °C (i.e., 180 °C)<sup>1</sup>. All life data except for Grease F and H which list in Table 6 were plotted on Figure

4 to make a correlation with a PDSC kinetic model. Equation 10 is a grease life equation developed with induction time (t) obtained at 180 °C. Its correlation coefficient ( $R^2$ ) was found to be 0.97. All predicted grease lives are listed in Table 7 with their ASTM D 3527 data. It shows that they have a good agreement.

$$\text{Grease High Temperature Life (hr)} = 177 t^{0.31} \quad [10]$$

In reviewing the test data, it was found that PDSC results from Grease F and H did not correlate to those of the ASTM D 3527 test. Table 6 clearly shows that Grease F provided a long induction (32 hrs), while it had a short life in the ASTM D 3527 test (100 hr). Generally, a long induction provides a long grease life in the ASTM D 3527 test because of its good oxidation stability. Grease H and I show same result in the ASTM D 3527. It appears that the poor thermal stability may contribute to the grease life of a bearing. To investigate these results, all samples were tested at 180 °C according to the ASTM D 6184, Oil Separation from Lubricating Grease (Conical Sieve Method). The test results are summarized in Table 6 and clearly indicated that Grease F and H had excessive oil separations at the test temperature. The excessive oil separation can create the insufficient amount of grease in a bearing and leads a shorter high temperature life in the ASTM D 3527 test due to its dynamic open bearing system. Even though grease demonstrates excellent oxidation stability (i.e., long induction time) in the PDSC test, it does not necessarily translate to having a long high temperature life if the grease has a thermal stability problem including excessive oil separation or high evaporation loss at a given test temperature. In addition, their testing environments are not same. The PDSC test is a static test that can also measure induction time even if the oil was separated from grease, while the ASTM D 3527 is a dynamic bearing test that is not designed for oil lubrication. For these reasons, some of greases do not provide a good correlation between their PDSC data and those of the ASTM D3527 test. If greases having more than 30 % of oil separation at 180 °C, the equation 9 may not be applicable to predict their high temperature life.

## CONCLUSIONS

A PDSC kinetic model was developed based on the activation energy and first-order rate equation. This kinetic model can predict induction times and reaction rate constants at various temperatures. Its correlation coefficient is 0.99 when compared with actual data. In addition, it also calculates the degree of oxidation on degraded grease. The advantage of this kinetic model is that it can evaluate grease conditions and predict the grease oxidation life within a short period.

A correlation equation was also developed between PDSC data and those obtained from the ASTM D 3527 test. They gave a good correlation and the equation has a capability to predict the ASTM D 3527 grease life using an induction time that was generated at 180 °C. However, this equation has a limitation on grease having excessive oil separation or poor thermal stability.

Therefore, this kinetic model can be effectively used, with the ASTM D 5483 test method, in quality control, the evaluation of field samples, and in the research and development of new products.

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Table 1. Grease Identification and Physical Properties

Code	Grease	Base oil Type	Thickener	NLGI Consistency Number	Dropping Point, C	Evaporation Loss @ 180 C, %
A	Automotive Grease	PAO +Mineral	Li-complex	2	256	6.5
B	Aviation Grease	PAO	Clay	2	343	3.5
C	Industrial Grease	PAO	Polyurea	2	213	2.0
D	Precision bearing Grease	Ester	Li-complex	3	273	2.4
E	Precision Bearing Grease	PAO	Lithium	3	194	5.0
F	Instrument Bearing Grease	Ester	Lithium	2	187	11.7
G	NLGI EP Reference Grease, Batch 6	Mineral	Lithium	2	200	20.3
H	Biodegradable Grease	Polyol Ester + PAO	Li-complex	2	267	7.7
I	NLGI Reference Grease Batch 10	Mineral	Lithium	2	194	22.0
J	Electric Motor Grease	Mineral	Polyurea	2	253	1.6

Table 2. Induction Times from PDSC at Various Temperatures

Temperature (°C)	Grease A (min)	Grease B (min)
220	-	10.9
210	3.3	28.4
200	7.4	102.7
190	15.2	218
180	35.8	648
170	98.7	-

Table 3. Predicted Induction Times of Greases from Kinetic Model

Grease	Induction time 1, min	Induction time 2, min	$K_o$	Slope (E/R)	Activation Energy (E), KJ/mol	Predicted induction time, min, 180 C
A	35.8@180C	15.2 @190C	$2.16 \times 10^{16}$	17.967	149.4	35.8
B	28.4 @210C	10.9 @220C	$5.43 \times 10^{19}$	22,826	190.0	648.3
C	50.1 @210C	21.3 @220C	$1.89 \times 10^{17}$	20,366	169.3	817.7
D	11.5 @210C	5.4 @220 C	$8.54 \times 10^{15}$	18,159	151.0	138.3
E	78.7 @180C	6.4 @210C	$2.02 \times 10^{16}$	18,293	152.1	78.7
F	15.4 @210C	71.8 @200C	$1.30 \times 10^{31}$	35,189	292.6	1,917
G	74.3 @180C	18.8 @210C	$2.57 \times 10^8$	10,032	83.4	74.3
H	15.2 @210C	92.9 @180C	$2.26 \times 10^{11}$	13,204	109.8	92.9
I	44.7 @180C	18.5 @190C	$5.16 \times 10^{16}$	18,461	153.5	44.7
J	104 @190	24.9 @210C	$4.57 \times 10^{13}$	16,006	133.1	223.2

Table 4. The Predicted Induction Times of Grease A

Sample Name	Grease A	
Induction time	15.2 min	35.8 min
Test Temperature	190 °C	180 °C
Activation Energy, KJ/mol	149.4	
Slope (E/R)	179,673	
Frequency factor (ko)	2.15 E+16	
Temperature, °C	Rate constant (k), min <sup>-1</sup>	Induction Time, min
100	0.000	177151.3
110	0.000	50365.5
120	0.000	15265.9
130	0.001	4909.4
140	0.003	1668.0
150	0.008	596.4
160	0.021	223.6
170	0.052	87.6
180	0.128	35.8
190	0.303	15.2
200	0.687	6.7
210	1.509	3.0

Table 5. Oxidation Conversion of Grease A at 180 °C

Fractional Conversion (%)	Induction Time (min)
10.0	0.820
20.0	1.737
30.0	2.776
40.0	3.976
50.0	5.394
60.0	7.131
70.0	9.370
80.0	12.526
90.0	17.920
91.0	18.740
92.0	19.657
93.0	20.696
94.0	21.896
95.0	23.315
96.0	25.051
97.0	27.290
98.0	30.446
99.0	35.840

Table 6. Grease High Temperature Life and Their Induction Times

Sample	ASTM D 3527, hr	Induction Time @ 180 C, hr
A	151	0.6
B	340	10.8
C	400	13.6
D	240	2.3
E	171	1.3
F	100	32.0
G	192	1.2
H	20	1.5
I	160	0.7
J	287	3.7

Table 7. Comparison between Actual Grease Life and Predicted Grease Life

Sample	ASTM D 3527, hr	Predicted Grease Life, hr	Oil Separation @180 °C, %
A	151	150	25.9
B	340	368	2.9
C	400	395	4.4
D	240	228	13.2
E	171	191	12.0
F	100	515	82.3
G	192	186	12.7
H	20	200	31.8
I	40	158	52.9
J	287	266	3.6



